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entitled (54) **POLYACRYLATE FLOCCULANTS**

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Applicant (71) **THE DOW CHEMICAL COMPANY**

Actual Inventors (72) **HENRY VOLK and
PERCY JAY HAMLIN**

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The following statement is a full description of this invention, including the best method of performing it known
to us:

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Because it is readily polymerized and used extensively in polymerization reactions, acrylic acid has been the subject of numerous polymerization studies. Usually this monomer is polymerized as an acid. Previous studies have shown that increasing the pH of the acrylic acid polymerization system decreases both the degree and rate of polymerization. See for example, Kogyo Kagaku Zasshi, Journal Chemical Society, Japan, Industrial Chemical Section, Volume 58, pages 194-196 (1955).

Although acrylic acid can be polymerized to high molecular weight, flocculant grade polymers, it is necessary in the processing of the acidic polymerizate to mix a neutralizing reagent with the polymer gel. This is a difficult physical operation inasmuch as the aqueous polymerizates are very viscous and not readily mixed with other reagents, such as sodium potassium or ammonium hydroxides.

It would be particularly desirable to provide an improved process for the preparation of alkali metal polyacrylates whereby faster conversion rates are obtained. Especially desirable are polymers characterized by high molecular weights and efficient flocculation utilities.

The instant invention is directed to the above ends and involves polymerizing an ammonium or an alkali metal acrylate, e.g., ammonium, sodium or potassium acrylates and ammonium, sodium or potassium methacrylates, in water solution under specially controlled reaction conditions.

In the practice of the polymerization process of the invention, monomer concentration is maintained within the range from about 10 weight percent of the polymerization system up to about the monomer saturation level and preferably from about 20 to about 35 weight percent of the aqueous polymerization charge. For alkali metal acrylates, this solution is adjusted to at least

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about pH 10.7 by the addition of an alkali metal hydroxide. When polymerizing ammonium acrylates, at least 0.1 weight percent ammonium hydroxide is incorporated into the polymerization system. Depending upon the monomer concentration, the upper limit on the amount of alkali metal hydroxide that can be added will range from about 15 to less than 1 weight percent, based on the total weight of the system, as the monomer concentration increases from about 10 to about 35 weight percent. When polymerizing ammonium acrylates, the maximum amount of ammonium hydroxide varies inversely from 15 to 5 weight percent for monomer concentrations ranging from 10 up to 40 weight percent. Polymerization is conducted at a temperature within the range from about 0° up to about 100°C., preferably from about 25°C. to about 60°C.

Although the process of the invention is essentially directed to the preparation of homopolymers of the alkali metal and ammonium acrylates other monomers compatible with the polymerization charge can be included in the polymerization system. Normally such comonomers will comprise a minor proportion, e.g., less than about 25 weight percent, of the monomer charge. Examples of suitable comonomers include sodium styrene sulfonate, sodium ethylene sulfonate, 2-sodioethylacrylate and maleate and vinyl acetate. In general any anionic or nonionic monomer which is soluble in the polymerization system and is not adversely affected by the high pH can be copolymerized with the acrylates in accordance with the invention.

Further improvement in the above described polymerization process is achieved by introducing into the polymerization system at least about 1 percent by weight of an alkali metal or ammonium salt such as sodium or potassium chloride or sulfate. Such salts yield polymers of even higher molecular weight and greater flocculation efficiencies. These salts are useful at

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concentrations up to and exceeding the saturation level for the given system.

The above described recipes are polymerized by known techniques. Most conveniently the reaction is carried out as a solution polymerization reaction in water. Alternate modes include suspension and emulsion polymerization techniques whereby the monomer solution is first prepared and then either suspended or emulsified in a water immiscible liquid such as an aromatic or aliphatic liquid hydrocarbon.

Initiation of polymerization is accomplished by purging the monomer system of inhibitory oxygen and applying suitable catalytic means, such as chemical free radical catalysts or high energy irradiation, including X-rays, gamma rays and high energy electrons. Suitable chemical catalysts include sodium persulfate, potassium persulfate, ammonium persulfate, azobisbutyronitrile, tertiary butyl-hydroperoxide and in general any of the peroxidic acid polymerization initiators not adversely affected by the high pH. Also operable are the redox initiator systems which involve the use of a reducing agent conjunctively with the oxidizing reagent.

Following completion of the polymerization reaction, the polymer is recovered by any convenient technique. When the polymerization is conducted in aqueous solution, the polymer may be recovered as by drum drying the polymerizate. Emulsion and suspension polymerization systems are well adapted for removing water by azeotropic distillation followed by a liquid-solids separation, as by filtering.

Polymers prepared in accordance with the invention are characterized by high molecular weights and good flocculation utilities. Those prepared in the presence of alkali metal hydroxides are especially efficient flocculants. Since molecular weight determinations are time consuming, a first approximation thereof is made by measuring the viscosity of a standard polymer solu-

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ution. For the purposes hereof, this determination is obtained on a 0.4 percent by volume solution of the polymer in 0.5 N NaCl at pH 8. The viscosity measurement is made with an Ostwald viscometer at 30°C. Polymers prepared in accordance with the invention are characterized by such a viscosity of at least 10 centipoises.

The instant invention will be further illustrated by reference to the following specific embodiments.

Example Series I

Freshly distilled acrylic acid, in an amount of 600 grams, was mixed with 1000 milliliters of water. The mixture was adjusted to pH 10.7 by the addition of 646 grams of about 50 percent aqueous caustic. A large portion of this was used in the neutralization of the acid. The resulting solution, which analyzed 34.33 percent by weight sodium acrylate was used for a series of polymer preparations at a constant monomer concentration of 30 percent but with varying amounts of additional caustic.

The polymerization recipes were charged to a one liter resin flask equipped with a stirrer, nitrogen sparger, gas outlet and thermometer. Air was removed from the monomer system by sparging with nitrogen. Sodium meta bisulfite was then added in an amount of 0.003 percent followed by potassium persulfate in an amount of 0.006 percent, said percentages being based on the weight of monomer. Each polymerization recipe was maintained throughout the polymerization within the range of 25° to 35°C. After 19 hours the polymerizations were terminated and the polymerizate analyzed for residual monomer. From this data, the conversions of monomer to polymer were calculated for each recipe.

The polymers were isolated from the polymerizates by precipitation with methanol. Volatiles were removed by drying at about 40°-50°C. in a vacuum oven. The viscosity of the dried

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product was determined using an Ostwald viscometer to measure 0.4 percent by volume polymer solutions in 0.5 normal sodium chloride.

The activity of the polymers as flocculants were determined by flocculation tests on a 10 percent by volume slurry of montmorillonite clay in 0.6 normal sodium hydroxide. The clay suspension was contained within a stoppered 100 milliliter graduate. The suspension was treated with an applying solution containing 0.025 weight percent of dissolved polymer at doses of 1, 2 and 3 milliliters. After mixing the polymer with the clay suspension according to a standard procedure, which involved rotating the graduate three times after introduction of the polymer, the lapsed time for the interface between the clarifying supernatant liquid and settling solids to descend from the 90 milliliter to the 60 milliliter mark was measured. These times are reported as the "flocculation times."

The recipes to prepare several polymers and the measurements of physical characteristics and flocculation times are reported as Runs 1-5 in Table I. Runs 6-10 in Table I were similar in every respect to the procedure described above except that the polymerizate was heated during the polymerization reaction over a temperature range from 23° to 40°C. and the reaction time was extended to 112 hours to obtain more complete conversions.

TABLE I

Polymerization Recipe

Run No.	Acrylate wt. %	Additional NaOH wt. %	Monomer Solution pH	Reaction Time	Temp. Conversion %	Monomer Conversion %	Viscosity cps.	Flocculation Times (Sec.)
1	30	None	10.6	19	Room T.	83.6	13.5	65 22 14.5
2	"	0.1	12.6	"	"	89.2	27.0	23 9 4.4
3	"	0.5	13.3	"	"	27.8	31.2	15 6.8 3.2
4	"	1.0	13.6	"	"	18.3	25.6	18.5 6.9 3.1
5	"	5.0		"	"	5.4	--	-- --
6*	"	None	10.4	112	23-40°C.	4.7	--	31.9 51.7
7	"	0.1	12.6	"	"	99.3	29.0	26 11 6.5
8	"	0.5	13.3	"	"	99.4	22.9	38 14 6.9
9	"	1.0	13.6	"	"	98.6	21.5	35 16 7.8
10	"	5.0	--	"	"	95.6	14.5	52 20 9.0

4* On occasion, there is failure to obtain effective initiation of the polymerization, when the pH of the monomer system is too low.

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It will be observed from the above data that a small amount of caustic in excess of that necessary to neutralize the acid monomer is necessary for successful results at high monomer concentrations. Compare Runs 1 and 6 with those following.

At such high monomer levels, the minimum pH is also critical. This was illustrated by the comparative polymerization of sodium acrylate at the monomer saturation level (approximately 38.2 weight percent at 30°C.) at pH 10.25 and in the presence of 0.1 weight percent caustic (pH > 10.7). At the lower caustic concentration, the polymer was essentially insoluble while at the higher level, a water-soluble, flocculant grade polymer was obtained. Preferably the amount of additional alkali is within the range from about 0.01 up to about 1.0 percent by weight, based on the polymerization system, i.e., the alkali acrylate monomer solution.

Example Series II

In a manner similar to the procedure employed above, series of polymerizations were conducted at each of 5, 10 and 20 weight percent monomer concentrations. A redox catalyst system comprising potassium persulfate and sodium bisulfite in a 2/1 weight ratio was employed at levels of from about 0.009 to about 0.0375 weight percent based on monomer. As monomer increased in concentration, the amount of catalyst was reduced. The temperature during polymerization ranged from room temperature to 35°C. Polymers were prepared in the above manner with varying amounts of caustic ranging from an amount just sufficient to produce a pH of 10.7 up to an amount at which levels the polymerization characteristics began to deteriorate.

High viscosity flocculant grade polymers were only obtained in polymerizations at 10 and 20 weight percent monomer levels. At 10 % monomer, the minimum amount of sodium hydroxide

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needed to prepare such polymers was 4%. At 20 weight percent monomer, the minimum sodium hydroxide was 1.5%. At 25% monomer up to 35% monomer concentrations, satisfactory high viscosity, flocculant polymers were obtained at pH levels above pH 10.7. The upper limit on sodium hydroxide ranged downwardly from 15% at 10% monomer, 9% at 20% monomer and 3% at 30% monomer.

Example Series III

In a manner similar to the polymerization mode employed in Series I, sodium acrylate was polymerized at 20 weight percent in water, with and without the addition of additional caustic. Polymerization times, temperatures and the amount of catalyst were controlled to provide a comparative showing of the effect of the additional caustic on conversions. The results as well as the particular polymerization conditions employed are set forth in the following Table II.

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TABLE II

Run	Sodium Acrylate Wt. %	% NaOH	% NaCl	pH	% Catalyst	Polymerization Time (Hours)	Polymerization Temperature (°C.)	Monomer Conversion (%)
1	20	--	--	9.0	0.018	72	35°	40.1
2	"	5	--	13.9	"	"	"	95
3	"	--	--	9.2	0.018	50	35°	0
4	"	5	--	13.9	"	"	"	98.5
5	"	--	5	9.4	0.018	20	"	36
6	"	1	" ~ 13	"	"	"	"	93

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From the above data it will be apparent that the addition of sodium hydroxide gives a substantial improvement in conversion of monomer to polymer. Run 2 which contained 5 percent sodium hydroxide based on charge weight (pH 13.9) had a conversion of 95 percent while Run 1 which was polymerized at the same conditions but at pH 9.0 was converted only to the extent of 40.1 percent. Similar comparisons are shown by Runs 3 and 4 and also 5 and 6.

Example Series IV

Freshly distilled acrylic acid in an amount of 76.6 grams was mixed with a solution of 168.7 grams of 28 percent ammonium hydroxide in 153 grams of water and the mixture was charged to a one liter resin flask equipped with a stirrer, nitrogen sparger, gas outlet and thermometer. Air was removed from the monomer system by sparging with nitrogen. Polymerization was initiated at room temperature by the addition of sodium meta bisulfite in an amount of 0.003 percent followed by potassium persulfate in an amount of 0.006 percent, said percentages being based on the weight of ammonium acrylate.

Also prepared in an essentially similar manner were polymerization systems containing different levels of ammonium hydroxide. Polymerization was carried out at ambient room temperature and the polymerizates analyzed for residual monomer. From this data, the conversions of monomer to polymer were calculated for each recipe.

The polymers were isolated from the polymerizates by precipitation with methanol. Volatiles were removed by drying at about 40°-50°C. in a vacuum oven. The viscosity of the dried product was determined using an Ostwald viscometer to measure 0.4 percent by volume polymer solutions in 0.5 normal sodium chloride.

The recipes to prepare several polymers and the measurements of physical characteristics and flocculation times are reported in the following Table III.

TABLE III

Run	Polymerization Conditions						Results					
	% NH ₄ Acrylate	Wt. % K ₂ S ₂ O ₈	Wt. % Na ₂ S ₂ O ₅	% NH ₃ Excess	Time Hrs.	Temp. °C.	pH	Conv. %	Visc. (cps)	Dose 1 ml.	Dose 2 ml.	Dose 3 ml.
Example 1	23.0	.003	.0015	None	40	*22-25	7.5	54.6	9.8	--	112	72
2	23.67	.005	.0025	7.3	20	"	9.9	83	24	34	17	8
3	"	"	"	9.3	"	"	10.1	74	29.1	31	14	8
4	"	"	"	18.1	"	"	10.6	20	--	--	--	--
5	30	.01	.005	None	"	"	7.0	81.9	49.9	21.3	--	--
6	"	"	"	0.1	"	"	7.22	86.5	38.2	31.7	--	--
7	"	"	"	1.0	"	"	8.75	96.0	48.7	31.5	--	--

* Room Temperature

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It will be observed from Runs 2 through 3, as compared to Run 1, that superior results were obtained in regard to conversion of monomer to polymer, molecular weight and flocculation when the ammonia concentration was properly adjusted. The results from Run 4 demonstrate the effect of an excessive concentration of ammonium hydroxide. In this run the conversion of monomer to polymer was less than 20 percent.

In Runs 5, 6 and 7, 30 percent by weight based on total solution weight of ammonium acrylate was polymerized in the presence of essentially none, 0.1 and 1.0 percent based on total solution weight of ammonium hydroxide. Although such small amounts of ammonium hydroxide gave no apparent advantage as regards polymer viscosity and flocculation properties, increased conversion to polymer did result.

Although the invention has been illustrated by solution polymerization techniques, it should be understood that other modes of polymerization may incorporate the improvements and advantages of the instant invention. For instance, inverse emulsion and bead suspension polymerization techniques may be carried out utilizing monomer solutions in which the monomer concentration and solution pH are adjusted in accordance with the parameters of the instant invention. Basically, in these polymerization techniques the monomer solution is suspended in a heat transfer medium with either an emulsifying or polymeric suspending agent. Details as to such suspension techniques are set forth in U. S. Patents 3,211,708, 3,278,506 and 3,284,393.

Depending upon the particular polymerization technique utilized, the polymer may be simply recovered from the polymerizate as by drying the polymerizate to recover the polymer solids. More conveniently, precipitation and, in the instance of the emulsion and suspension polymerization techniques, precipitation or

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azeotropic drying followed by filtration of the polymer solids from the polymerization medium may be employed to recover polymer solids. It should be understood, however, that separation of the polymer solids is not necessary to their useful application. For instance, the polymer gels and suspensions thereof can be directly employed to prepare polymer applying solutions and, in some instances, the emulsion polymer systems can be applied as flocculants without prior dilution.

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The claims defining the invention are as follows:

-1-

A method for preparing alkali metal and ammonium polyacrylates which comprises:

- (1) forming an aqueous solution containing from 10 percent by weight to the monomer saturation level of dissolved alkali metal or ammonium acrylate or methacrylate and ^{either (a)} an effective amount of alkali metal hydroxide sufficient to impart to this solution a pH of at least 10.7, or ^{(b) in the event ammonium acrylate or methacrylate is being polymerized, at} least 0.1 percent ammonium hydroxide based on the weight of the monomer solution, and
- (2) purging the monomer solution of inhibitory oxygen and
- (3) polymerizing the resulting monomer system at a temperature within the range from about 0° up to 100°C. in the presence of a polymerization catalyst.

-2-

The method of Claim 1 and including the additional step of separating the polymer from the polymerizate.

-3-

The method of either Claim 1 or 2 wherein the acrylate concentration is within the range from about 20 to 35 percent by weight of the total polymerization system and a high molecular weight polymer is recovered from the polymerization system.

-4-

The method of Claims 1, 2 or 3 wherein sodium acrylate is polymerized in the presence of sodium hydroxide.

-5-

The method of Claims 1, 2 or 3 wherein ammonium acrylate is polymerized in the presence of ammonium hydroxide.

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-6-

The method of Claims 1, 2 or 3 wherein an alkali metal acrylate is polymerized at a monomer concentration within the range of 20 to 35 weight percent and the amount of additional alkali metal hydroxide is within the range of 0.01 up to 1 percent by weight of the polymerization system.

-7-

The method of Claims 1, 2 or 3 wherein an ammonium acrylate is polymerized at a monomer concentration within the range of 10 to 40 weight percent and the amount of ammonium hydroxide is within the range of 1 to 15 percent by weight of the polymerization system.

-8-

The method of Claims 1, 2 or 3 wherein the monomer charge contains up to 25 weight percent of another anionic or nonionic monomer.

-9-

The method of Claims 1-8 wherein the monomer solution is emulsified or suspended in an inert liquid reaction medium prior to initiating polymerization.

-10-

The method of Claims 1, 2 or 3 and including the additional step of introducing from about 1 percent by weight up to its saturation level of an alkali metal inorganic salt to the polymerization charge.

-11-

The method of Claim 9 wherein the salt is sodium chloride.

-12-

The method of Claim 9 wherein the salt is sodium sulfate.

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13. A method as claimed in claim 1 substantially as herein described with reference to any one of the Examples.

14. A polymeric product prepared by anyone of the methods of claims 1 - 13.

DATED: 2nd August, 1974.

PHILLIPS ORMONDE AND FITZPATRICK
Attorneys for :-
THE DOW CHEMICAL COMPANY

David Fitzpatrick



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